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THE ELECTRICAL PROPERTIES OF THE INORGANIC PAPERS

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ABSTRACT

The electrical properties of asbestos, mica, ceramic, glass, and silica fiber papers have been studied for possible use as thermally stable insulants.

The dielectric constants of the synthetic fiber inorganic papers are of the order of 1.05 - 1.15; the densities are correspondingly low (0.2 - 0.3 gm/cc). The dielectric constants of the naturally occurring inorganic papers are higher (3.5) due to the correspondingly higher densities. The electrical losses are lowest in the synthetic base papers (0.0001) and highest in the asbestos products (0.6).

PROBLEM STATUS

This is an interim report on the problem; work is continuing.

AUTHORIZATION

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INTRODUCTION

The demand for reliability in electrical equipment under severe conditions of temperature and weather has necessitated the development of papers having insulating qualities and thermal stabilities far above those found in rope and wood-pulp products.

Two approaches (Table 1) to the solution of the problem have been investigated; the one involving the beneficiation and modification of naturally occurring paper-forming inorganic materials, and the other, the preparation, synthetically, of fine inorganic fibers suitable for paper making. In the first category, asbestos, bentonite, and mica are found, while glass fiber, ceramic fiber, and silica fiber occur in the latter.

TABLE 1
Inorganic Papers

Natural Base			Synthetic Base		
Asbestos	Bentonite	Mica	Glass	Ceramic	Silica
Terratex	Diaplex	Integrated Mica	Hurlbut	NBS	Hurlbut
Quinterra		Samica	Microtex		
Novabestos		Micamat	U.S. Machine & Foundry		

The work of Hauser and Reed (1) indicated that the purification of natural film-forming inorganic bodies, such as bentonite clay, resulted in nonflammable electrical insulants. While these films, because of their continuity, possessed dielectric strengths superior to those of the better varnishes, unfortunately they lacked the toughness, flexibility, and tear strength requisite for handling in wire and cable capsans. Some commercial exploitation of these films in the capacitor field was undertaken by Rohm & Haas under the trade name of "Diaplex"; this product has not been developed as widely as had been expected.

ASBESTOS PAPER

Recognizing the deficiency of the films, Walters (2) developed the bentonite-modified asbestos papers called "Terratex," while Quinn's work (3) resulted in the presently available "Quinterra" and Quinorgo of commerce. Modifications of these types (4) including

"Novabestos" have been disclosed. The asbestos papers found their immediate use in the air-cooled transformers and reactors rated for operation at elevated temperatures and under conditions where the liquid cooled counterpart is unsuitable.

In the early stages of the work, the apparent solution of the problem of a thermally stable dielectric paper rested on the availability of high-grade magnetite-free chrysotile asbestos. World War II demonstrated glaringly the absolute need for (a) techniques for purifying the asbestos of Canada, (b) re-opening the Arizona deposits, or (c) finding other inorganic dielectrics based on materials indigenous to the United States.

MICA PAPER

At the same time that the shortage of electrical-grade asbestos was alarming the logistics experts, the mica problem had become acute. Although many thought the problem to be a mica shortage per se – as there was an asbestos shortage – actually, the shortage was one of labor supply. Accurately evaluating this, Heyman (5) began his studies on mechanically splitting mica; his work resulted in "Integrated Mica" (6). Bardet's work (7) on the chemical pulping of mica has resulted in mica paper preparable on a modified Fourdrinier machine (8). To a paper maker the two developments correspond to mechanical vs. chemical pulping. These latter products are available in the United States now under the trade names of "Samica" (9) and "Mica Mat" (10).

The dielectric constant (ϵ'), power factor (% P.F.), and dielectric loss factor (ϵ'') at 60, 1000, and 10,000 cycles are given in Figures 1 and 2 for asbestos and mica paper. The asbestos paper was prepared at NRL by passing beaten Canadian chrysotile (Grade-3Z) through a Nichols Vortrap, followed by formation in a sheet mold according to TAPPI standards. Analysis indicated the asbestos to be magnetite free. The mica paper was prepared by circulating North Carolina scrap muscovite in a paper beater, removing the dispersed mica flakes suspended near the top of the stock, furnishing this to a laboratory sheet mold, and forming a piece of paper by TAPPI methods. In neither case were commercial items used because all samples submitted to the author by the manufacturers contained organic binders. Data on the commercial items may be obtained directly from the producers.

Examination of the graphs reveals that the apparent dielectric constant of asbestos is from three to five times greater than that of mica paper under similar conditions of temperature, voltage gradient, and frequency. The electrical losses are seen to be one hundred to five hundred times greater under the conditions employed. These losses contribute appreciably to the apparent dielectric constant according to the classical equation, $\epsilon' = \epsilon + j\epsilon''$; the densities of the papers differ also – another source of differing total polarizability. This is substantiated by the marked difference in the 60-cycle and the 10,000-cycle data. At the higher frequency, the ionic component of the apparent dielectric constant has been reduced appreciably resulting in a value only twice that of mica paper. Similarly the slope of the curve over the thermal range studied is lessened considerably.

It has been suggested that these losses in the asbestos arise from the chemically reactive brucite in the fiber. Modification of the magnesium hydroxide by reaction with acid halides or by thermal degradation suggests itself (11).

SYNTHETIC FIBER PAPERS

Chemically, the natural and synthetic paper-making materials for inorganic papers are best distinguished as shown in Table 2. It can be seen that the items on the left-hand side of the figure are the glass formers or high-melting items, silica melting at 1710 and corundum (alumina) at 2000 degrees centigrade. On the right-hand side of the figure, the

network modifiers are indicated. These materials tend to lower the melting point of the material, necessary in the case of economic glass fiber spinning, undesirable in the case of the natural hydrous bodies (asbestos, mica, and bentonite).

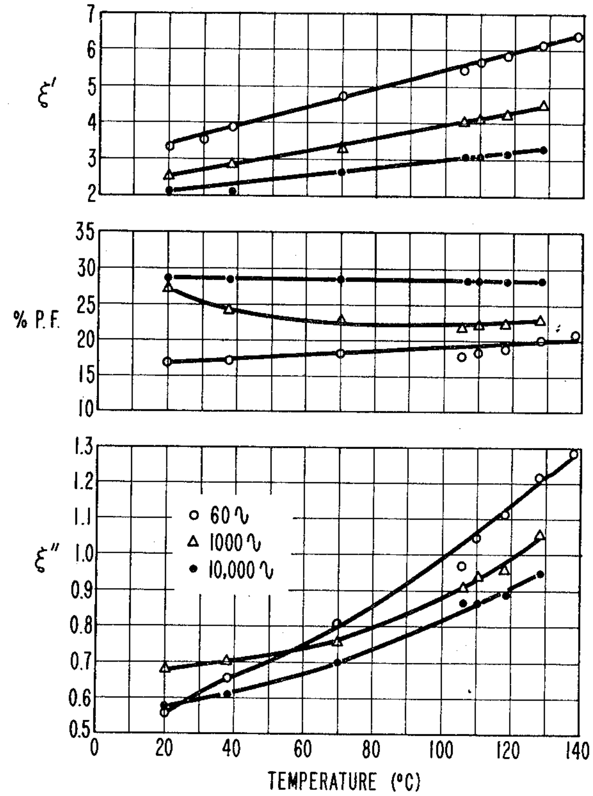

Figure 1 - The electrical properties of asbestos paper

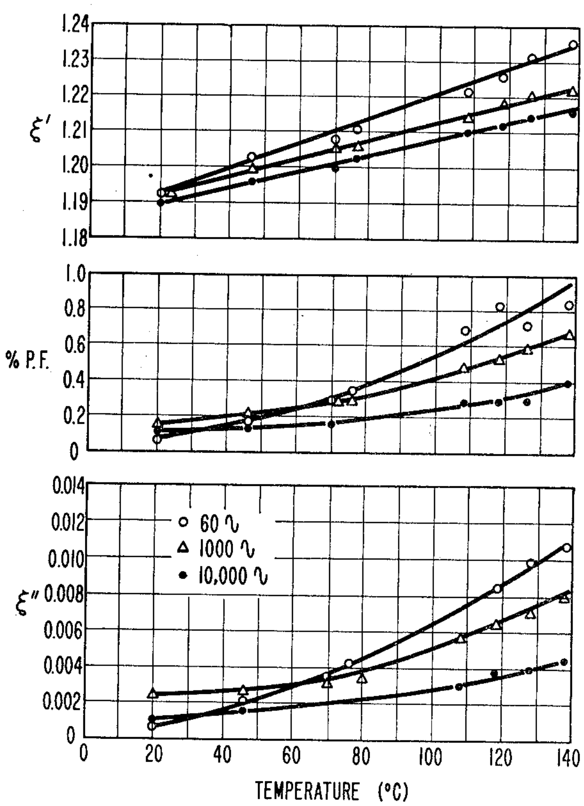

Figure 2 - The electrical properties of mica paper

TABLE 2
Chemistry of the Inorganic Papers

Inorganic Papers	Network Formers			Network Modifiers				
Silica	SiO_2	-	-	-	-	-	-	
Ceramic	SiO_2	Al_2O_3	-	-	-	-	-	
Bentonite	SiO_2	Al_2O_3	-	H_2O	-	Na_2O	-	
Mica	SiO_2	Al_2O_3	-	H_2O	K_2O	-	-	
Asbestos	SiO_2	-	-	H_2O	-	-	MgO	
Glass	SiO_2	Al_2O_3	B_2O_3	-	K_2O	Na_2O	MgO	CaO

The exploitation of the synthetic inorganic fibers as paper-making pulps has increased appreciably during the last year (12) due to the commercial availability of glass fibers from Glass Fibers, Incorporated, Waterville, Ohio and Owens-Corning Fiberglas Corporation, Toledo, Ohio; of ceramic fibers from the Carborundum Company, Niagara Falls, New York; and of silica fibers from the H. I. Thompson Company, Los Angeles and Glass Fibers, Incorporated.

Since all three types of fibers are available commercially in diameters of 2 microns, and in the cases of glass and silica as low as 0.2 micron, the fibers may be handled as a water-dispersed paper stock in commercial equipment without modification. Fibers of greater diameters tend to settle in the paper-making system and are not commercially feasible at this time. Again the fine fibers permit the production of a paper of greater fiber density, and consequently of greater mechanical strength. At the present time, the papers are approximately one-tenth the density of the material from which the fibers were made. While it is apparent that the finer the diameter, the stronger the product produced, due to increased packing factor, the problem of spinning fibers which are both fine and long tends to put a practical limit on the finest diameter commercially suitable for exploitation. At present fibers having diameters of 0.2 micron are, on the average, 50 microns in length. Apparently the quality of the melts from which these fibers are blown can be changed to produce certain engineering improvements in the ratio of length to diameter. Also, as a pro tempore solution, the admixture of the fibers with filler clays such as bentonite, or with organic binders such as phenolics, melamines, neoprenes, and water-soluble cellulosates has resulted in the development of useful items.

The glass fiber art has reached the stage where the producer can ship the glass pulp in bales for processing. Similarly, the silica fiber is available as a bulk item. "Fiberfrax" is still in the developmental stage and must be sent through a refining system to remove the shot and slubs which form in any method of producing rock wool. Glass fibers, in general, are free from such slivers because of the melt spinning techniques employed (13). Silica fiber, which is produced by leaching and recovering glass fiber, is similarly free from such shot. In general, Vortraps or sand traps will clean a shot-laden pulp without difficulty.

The dielectric constant, dielectric loss factor, and percentage power factor have been plotted for three inorganic papers. Figure 3 contains data obtained from a 100-percent glass fiber sheet produced from Glass Fibers Incorporated material processed into paper on the experimental machine at the National Bureau of Standards. The second sheet (Figure 4) consists of mechanically strong paper produced by admixing bentonite clay with ceramic fiber in the weight ratio of 1:4 with a trace of copper sulfate as a precipitant. This sheet was also prepared as a pilot plant run in NBS. The third sheet of paper

(Figure 5) was prepared from leached but unfired silica fiber (analysis: 84.5% silica; 15.5% water) obtained from Glass Fibers Incorporated. After sending the fiber over the machine at the National Bureau of Standards and successfully making it into paper, the sheet was then fired at 600 degrees centigrade for 48 hours, and its electrical properties determined (Figure 6). Analysis indicated 96.5% silica, 0.5% soda, 1.3% alumina, and 1.7% ferric oxide.

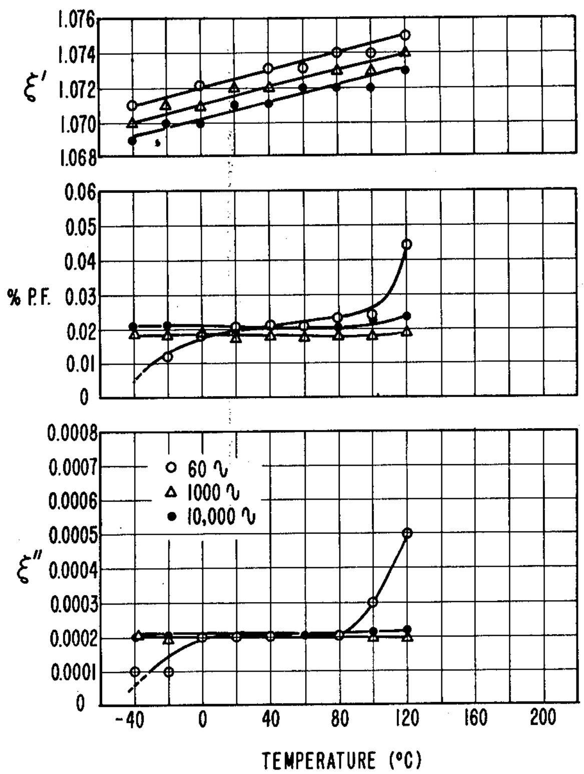

Figure 3 - The electrical properties of glass fiber paper

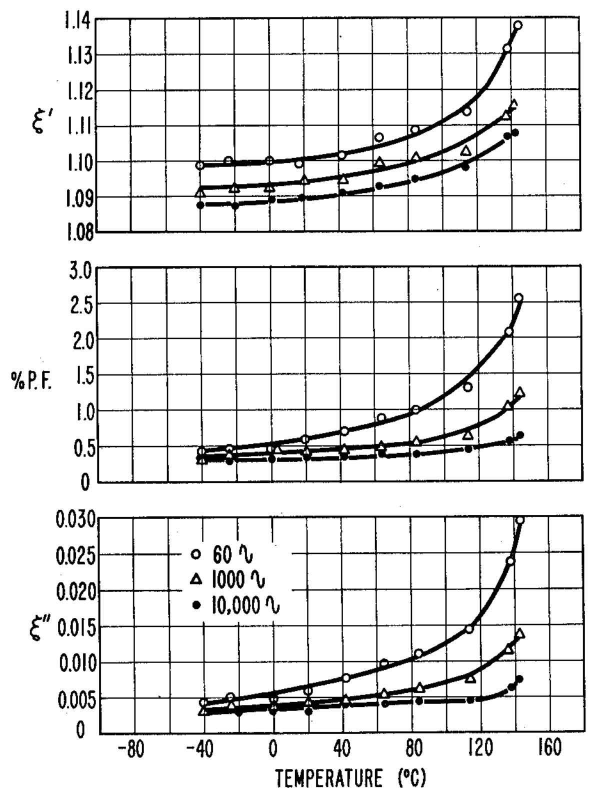

Figure 4 - The electrical properties of ceramic-fiber bentonite-clay paper

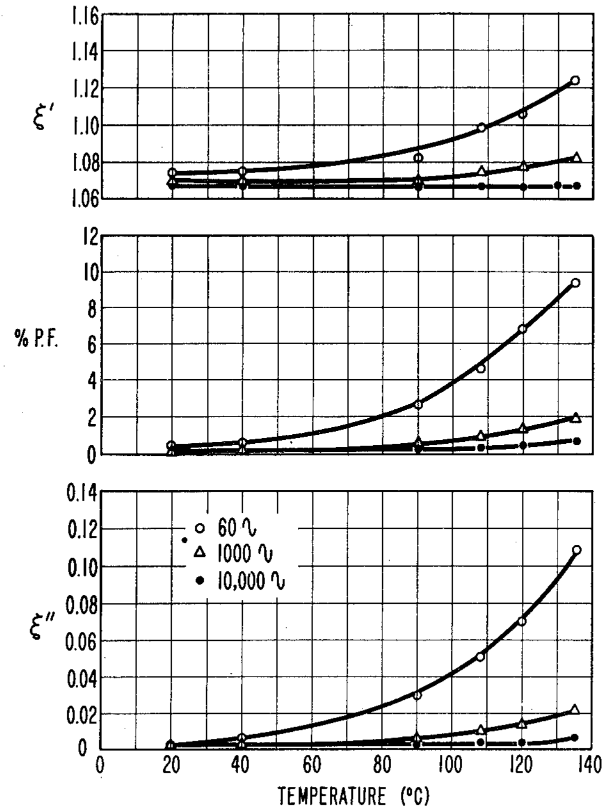

Figure 5 - The electrical properties of hydrous silica fiber paper

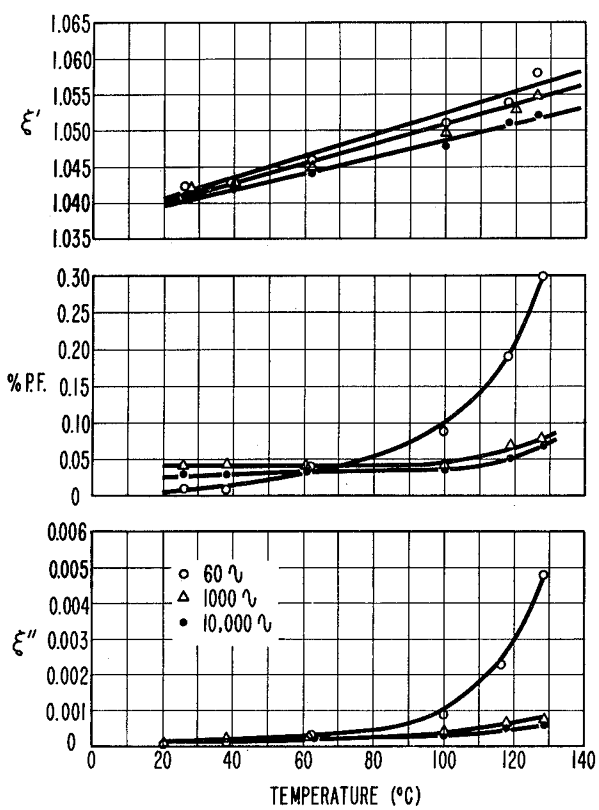

Figure 6 - The electrical properties of anhydrous silica fiber paper

Examination of the data indicates that the dielectric constants increase progressively from silica to glass to ceramic-bentonite paper. This is due to two things: the dielectric constants of the materials and the densities of the sheets. Thus, the silica and glass fiber papers have approximately the same densities (0.2 gm/cc); but pure silica has a dielectric constant of 3.85 and glass 6.31 under similar conditions of temperature, frequency, and voltage gradient. On the other hand the density of the ceramic-bentonite paper is twice that of the silica or glass papers studied, and, consequently, the dielectric constant is almost 5% higher – the dielectric constant of the base materials being 5.5 to 6.5.

The losses in all three papers develop run-away characteristics at elevated temperatures which have been interpreted to mean that there are present entrapped ions. All three papers were prepared using Washington, D. C. city water known to possess quantities of ions. Work with handsheets prepared from ion-free water has shown that no such run-away losses appear up to 150 degrees centigrade with either glass or silica fiber papers.

No commercial synthetic inorganic fiber papers were used in these tests because of the variety of techniques used by the various mills. The Hurlbut Paper Company, South Lee, Massachusetts has successfully made glass fiber paper. Whitehouse Paper Company, Philadelphia, Pennsylvania markets its glass paper under the trade name "Microtex." The Hartford City Paper Company, Hartford City, Indiana and C. H. Dexter Paper Company, Windsor Locks, Connecticut have also made glass paper from microfibers. The National Bureau of Standards has made paper from all three synthetic inorganic fibers.

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REFERENCES

1. Hauser, E. A., and Reed, C. E., "Studies on Thixotropy II. The Thixotropic Behavior and Structure of Bentonite," J. Phys. Chem. 41:911-34, 1937

2. Walters, T. R., "Insulating Paper of Asbestos and Bentonite," (to General Electric Company) U.S.P.2,493,604, 3 Jan. 1950

3. Harkness, J. C., and Quinn, R. G., "Dielectric Sheet," (to Johns-Manville Corp.) U.S.P.2,485,458, 18 Oct. 1949

4. Callinan, T. D., "Impregnating Asbestos with Tin Oxide," (to General Electric Co.) U.S.P.2,460,734, 1 Feb. 1949

5. Heyman, M. D., "Mica and Mica Substitutes – II," National Security Industrial Association, New York, New York

6. Heyman, M. D., "Integrated Mica and Method of Making Same," U.S.P.2,405,576, 13 Aug. 1946

7. Bardet, J. J., "Methods for Treating Mica and Composition," U.S.P.2,549,880, 24 Apr. 1951

8. George, H., and Metzger, L., "Le Papier de Mica 'Samica'," Revue Generale de L'Electricite 59:519-524, Dec. 1950

9. Griffeth, R. L., and Younglove, E. R., "The Manufacture and Processing of Mica Paper for use in Electric Insulation," A.I.E.E., Winter Meeting, 21 Jan. 1952

10. Kern, E. A., Letteron, H. A., and Staats, P. L., "Mica Mat," G. E. Review 55: No. 3, p. 54, May 1952

11. Callinan, T. D., "Coating Asbestos," (to General Electric Co.) U.S.P.2,451,805, 18 Oct. 1948

12. Callinan, T. D., Lucas, R. T., and Bowers, R. C., "The Electrical Properties of Glass-Fiber Paper," Elec. Mfg. 48:94-97, Aug. 1951

13. Barnard, R. H., "Glass Fiber Production," Electrified Industry, p. 24, Feb. 1950

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